Novel Lewis Acid Promoted Reactions of Allylsilane Bearing Bulky Silyl Substituents and Aldehydes

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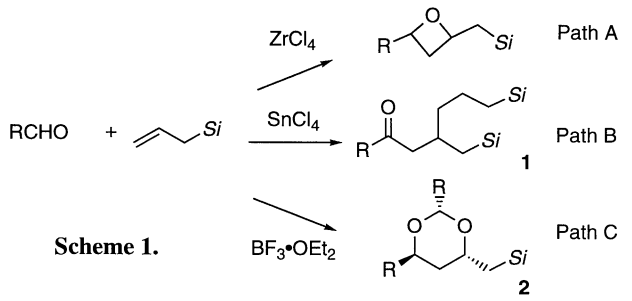
Reported herein are two novel modes of reactions that were mediated by the proper choice of Lewis acid. Thus, by the influence of $SnCl_4$, allyl-*t*-butyldimethylsilane reacted with aldehyde in 2:1 stoichiometry to afford a ketone derivative. In contrast, use of BF_3•OEt_2 led to the formation of a 1,3-dioxane derivative, which is a 1:2 adduct.

Lewis acid promoted allylation of carbonyl compounds with allylsilane has been utilized as an efficient method for the preparation of homoallyl alcohols.[1,2] Although the Sakurai reaction enjoys wide application in organic synthesis, one sometimes encounters anomalous products; 4-halotetrahydropyran derivatives were obtained by $AlCl_3$ promoted reaction of allylsilane and aldehyde.[3] Suzuki reported $NbCl_5$-promoted formation of cyclopropanes.[4]

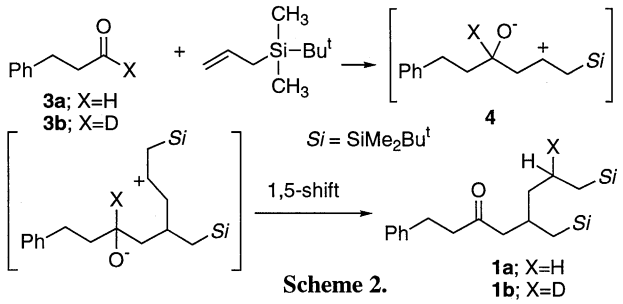
Recently allylsilanes bearing bulky silyl substituents have been reported to act as 1,3-dipole or 1,2-dipole equivalents; the reaction course depends on the substrate and the proper choice of the Lewis acid. Thus 5-membered[5] and 4-membered[6] carbocycles have been constructed stereoselectively by Lewis acid promoted cycloaddition of allylsilane with α,β-unsaturated carbonyl compounds. Cycloaddition reaction of the allylsilane with carbonyl compounds afforded 5-membered[7] and 4-membered heterocycles.[8]

We reported that $ZrCl_4$ promoted [2+2] cycloaddition of allylsilane bearing sterically demanding silyl substituents and aldehyde furnished oxetanes in good yields (Scheme 1, Path A).[9] We wish to disclose herein that two novel modes of reactions were realized by the proper choice of the Lewis acid. Thus, by the influence of $SnCl_4$, allyl-*t*-butyldimethylsilane reacted with aldehyde in 2:1 stoichiometry to afford ketone derivative (**1**) (Path B). In contrast, use of BF_3•OEt_2 led to the formation of 1,3-dioxane derivative (**2**), which is a 1:2 adduct (Path C).

At the outset, addition of tin(IV) chloride (1.2 equiv) to a solution of allyl-*t*-butyldimethylsilane (1.2 equiv) and 3-phenylpropanal (**3a**) (1.0 equiv) in CH_2Cl_2 at –78 °C for 8 min led to quick consumption of **3a**. Corresponding homoallyl alcohol, Sakurai product, was not observed and a ketone derivative (**1a**) was obtained in 64% yield.[10] Its structure was determined by IR and ^1H, ^{13}C, 2D-COSY, and HMQC NMR



Scheme 1.



Scheme 2.

experiments.[11] The formation of **1a** is rationalized by the mechanism shown in Scheme 2. Nucleophilic attack of the allylsilane to aldehyde gave a β-carbocation intermediate (**4**). Another allylsilane attacked the β-silyl carbocation and subsequent 1,5-hydride shift afforded **1a**. To confirm the mechanism, deuterium labeled aldehyde (**3b**) was employed as a substrate. As expected, corresponding β-silyl deuterio compound (**1b**) was obtained in a good yield. It is noted that present reaction took place only when allylsilanes bearing sterically demanding silyl substituents were employed:[12] allylsilanes bearing small silyl group such as (*Si* =$SiMe_3$, $SiMe_2Ph$, $SiPh_3$) afforded only Sakurai product and formation of **1** was not observed under the identical reaction conditions.

Next, treatment of allyl-*t*-butyldimethylsilane (1.0 equiv) and 3-phenylpropanal (2.0 equiv) with BF_3•OEt_2 (1.0 equiv) in CH_2Cl_2 at –78 °C for 15 min led to the formation of a dioxane (**2a**; R=$PhCH_2CH_2$, *Si* =$SiMe_2Bu^t$) as a single diastereomer in 72% yield (Table 1, Entry 1).[13] The relative stereochemistry was determined by *J* value as well as multiple NOE ^1H NMR experiments (Scheme 3). Formation of **2** is explained by attack of alkoxide anion to aldehyde, followed by the resultant alkoxide anion to β-silyl carbocation (Scheme 4).

Aliphatic aldehydes afforded the corresponding adducts in

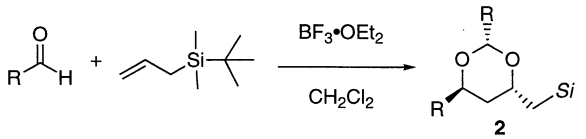
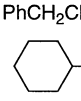
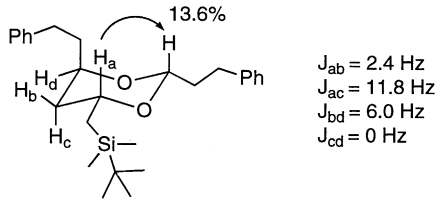
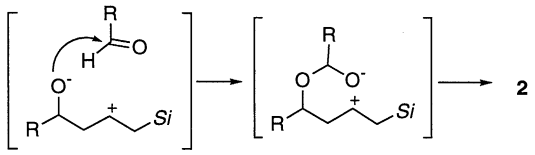


Table 1. BF_3•OEt_2 promoted reaction with several aldehydes

Entry	R	Yield of dioxane/%
1	$PhCH_2CH_2$-	73
2		57
3	$CH_3(CH_2)_4$-	57
4	C_6H_5-	13



Scheme 3. NOE correlation and J value of ^{1}H NMR.



Scheme 4.

good to moderate yields (Entries 1-3). An aromatic aldehyde showed less satisfactory result.

Present dioxane formation reaction also required allylsilanes bearing bulky silyl substituents; yields of the BF_3•OEt_2 promoted dioxane formation with 3-phenylpropanal are as follows; (*Si* = Si(*i*-Pr)$_3$; 51%, $SiPh_2Bu^t$; 32%, $SiPh_3$; 0%, $SiMe_2Ph$; 0%, $SiMe_3$; 0%).

Two novel modes of reactions were disclosed for the Lewis acid promoted reaction of allylsilane bearing bulky silyl substituents and aldehydes. At present, although the reason $SnCl_4$ and BF_3•OEt_2 exerted completely different reaction course is not clear, we speculate that the O-anion of the borate (RO^-BF_3) in **4** is more nucleophilic toward aldehyde than that of the stannate (RO^-SnCl_4).

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10 The yield is based on the allylsilane. When $SnCl_4$, 3-phenylpropanal, and allyl-*t*-butyldimethylsilane were employed in the molar ratio of 1.2: 1.0: 2.0, **1a** was obtained in 48% yield.

11 Selected spectra of **1a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ= –0.09 (6H, s), –0.03 (6H, s), 0.38-0.48 (3H, m), 0.54 (1H, dd, J=10.8, 6.8 Hz), 0.84 (9H, s), 0.86 (9H, s), 1.18-1.30 (4H, m), 1.99-2.10 (1H, m), 2.25 (1H, dd, J=18.0, 6.4 Hz), 2.36 (1H, dd, J=18.0, 6.8 Hz), 2.68 (2H, t, J=7.7 Hz), 2.87 (2H, brt, J=8.0 Hz), 7.14-7.30 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ= –6.25 (CH_3 x 2), –5.34 (CH_3), –5.03(CH_3), 12.60 (CH_2), 16.52 ($\underline{C}(CH_3)_3$), 16.61 ($\underline{C}(CH_3)_3$), 17.53 (CH_2), 21.38 (CH_2), 26.45 ($C(\underline{C}H_3)_3$), 26.52 ($C(\underline{C}H_3)_3$), 29.75 (CH_2), 30.34 (CH), 41.57 (CH_2), 44.95 (CH_2), 51.07 (CH_2), 126.04, 128.30, 128.46, 141.17, and 209.95.

12 Allyltriisopropylsilane afforded the corresponding adduct in 23% yield.

13 Spectra of **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ= –0.02 (3H, s), 0.01 (3H, s), 0.76 (1H, dd, J=14.4, 6.4 Hz), 0.86 (9H, s), 0.95 (1H, dd, J=14.4, 8.0 Hz), 1.42 (1H, dd, J=13.2, 2.4 Hz), 1.65-1.75 (1H, m), 1.86-1.97 (3H, m), 2.31 (1H, dddd, J=14.5, 9.5, 9.5, 5.3 Hz), 2.63 (1H, ddd, J= 13.7, 9.5, 6.8 Hz), 2.70-2.80 (2H, m), 3.90 (1H, dddd, J=11.8, 8.4, 6.0, 2.8 Hz) 4.09 (1H, ddd, J= 9.5, 5.8, 5.8 Hz), 4.82 (1H, t, J= 5.2 Hz), 7.15-7.35 (10H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ= –5.34 (CH_3), –5.05 (CH_3), 16.45 (C), 20.81 (CH_2), 26.40 ($C(\underline{C}H_3)_3$), 30.41 (CH_2), 32.24 (CH_2), 32.56 (CH_2), 36.79 (CH_2), 37.68 (CH_2), 70.40 (CH), 71.55 (CH), 94.06 (CH), 125.77, 125.90, 128.36, 128.40, 128.44, 141.80.